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Cathode dependence of the open-circuit voltage of polymer:fullerene bulk heterojunction solar cells

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The open-circuit voltage (V_{OC}) of bulk-heterojunction solar cells based on [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) as electron acceptor and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene] (OC₁C₁₀-PPV) as an electron donor has been investigated. In contrast to the present understanding, it is now demonstrated that for non-ohmic contacts the experimental V_{OC} is determined by the work function difference of the electrodes. A total variation of more than 0.5 V of the V_{OC} was observed by variation of the negative electrode (cathode) work function. For ohmic contacts the V_{OC} is governed by the LUMO and HOMO levels of the acceptor and donor, respectively, which pin the Fermi levels of the cathode and anode. The band bending created by accumulated charges at an ohmic contact produce a considerable loss in V_{OC} of 0.2 V at room temperature. The experimentally observed voltage loss in V_{OC} of 0.38 V due to the presence of ohmic contacts at both interfaces strongly limits the maximum open-circuit voltage of OC₁C₁₀-PPV/PCBM solar cells. © 2003 American Institute of Physics. [DOI: 10.1063/1.1620683]

I. INTRODUCTION

Photovoltaic devices prepared from blends of conjugated polymers and fullerene derivatives are promising candidates for solar energy conversion due to their mechanical flexibility, lightweight, and potential low cost of fabrication of large areas.¹ The efficient photoresponse of these devices originates from the ultrafast electron transfer from the conjugated polymer (donor) to fullerene (acceptor).² Over the last few years, a sustained effort has been made to improve the device performance of organic solar cells based on methanofullerene [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) as electron acceptor and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene] (OC₁C₁₀-PPV) as an electron donor. The development of the bulk-heterojunction (BHJ) concept, as well as improving the solid state morphology of the components and that of the blend, has lead to power conversion efficiencies up to 2.5% under AM1.5 illumination for this specific donor-acceptor tandem.³

Essential parameters which determine the power conversion efficiency of thin film photovoltaic devices are the short-circuit current (J_{SC}), the open-circuit voltage (V_{OC}), and the fill factor. It has been shown that the J_{SC} is sensitive to the film morphology, solvent type, or deposition method.^{4,5} Formation of a bulk heterojunction by mixing the polymer (donor) and the fullerene (acceptor) lead to an enhancement of J_{SC} due to an increased interface area for charge separation. However, it is still much lower than the J_{SC} reported for inorganic devices. This lower photocurrent is mainly due to the spectral mismatch between the sunlight and the absorption spectrum of the polymers (and fullerenes) used, as well as the limited transport of the separated charge

carriers to the electrodes due to the low charge carrier mobility in organic materials.

On the other hand, organic solar cells produce quite respectable open-circuit voltages. It has been demonstrated that for a photodiode, based on a single layer of a conjugated polymer, the V_{OC} scales with the work function difference between electrodes, and thus follows the metal-insulator-metal (MIM) model.⁴ In bilayer devices made by electron- and hole-accepting polymers, the V_{OC} also scales linearly with the work function difference, however, with an additional contribution depending on the light intensity.⁶ This contribution is due to the accumulation of charge carriers at the organic/organic interface, giving rise to a diffusion current which must be compensated by a drift current at open circuit. In BHJ solar cells, a linear correlation of the V_{OC} with the reduction potential of the acceptor has been reported.⁷ The fact that a slope unity was obtained indicates a strong coupling of V_{OC} to the reduction strength of the acceptors. In case of ohmic contacts, meaning that the negative and positive electrodes match the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied (HOMO) level of the donor, respectively, such a correlation is expected. The maximum V_{OC} for this case is schematically indicated by V_{OC1} in Fig. 1 and is thus governed by the bulk material properties. In case of non-ohmic contacts, as is depicted in Fig. 1, a reduced V_{OC} with magnitude V_{OC2} is expected, according to the MIM model. However, a very weak variation of the V_{OC} of only 160 meV has been observed when varying the work function of the negative electrode from 5.1 eV (Au) to 2.9 eV (Ca).⁷ This deviation from the MIM model has been explained by pinning of the electrode Fermi level to the reduction potential of the fullerene. For the design of future solar cells it is important to understand whether the V_{OC} of BHJ devices can be adapted by the choice of the electrodes and whether the V_{OC}

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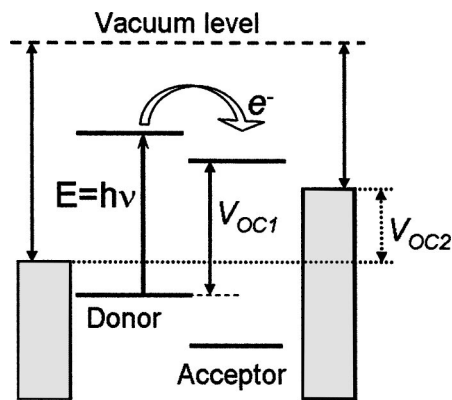


FIG. 1. Schematic variation of V_{OC} with acceptor strength (solid double headed arrow, V_{OC1}) or/and electrode work function (dotted arrow, V_{OC2}), in a donor/acceptor BHJ solar cell. The electron transfer, occurring at the donor/acceptor interface after light excitation, is indicated by the bent arrow.

is a bulk property (as shown by solid arrow in Fig. 1) or an electrode property (shown by dotted line in Fig. 1), or a combination of both. In the present study we first study the electronic properties of various negative top electrodes on PCBM-only devices. The information regarding the alignment of the Fermi level of the various electrodes on PCBM is then applied to the experimental data on OC_1C_{10} -PPV:PCBM based solar cells. We demonstrate that the V_{OC} of the cells can be varied over more than 0.5 eV by changing the work function of the top electrode.

II. RESULTS AND DISCUSSION

A. Open-circuit voltage of PCBM only device

In order to study a possible pinning of the Fermi level of the negative top electrode on PCBM, devices consisting of a single layer of PCBM were investigated as a reference. The devices were produced on top of a glass substrate, covered by indium-tin-oxide (ITO). As a bottom electrode, a hole transport layer of PEDOT:PSS (Bayer AG) was spin-coated under ambient condition, then the layer was dried in the oven. Subsequently, PCBM was spin cast from a chlorobenzene solution. Finally, gold (Au) (50 nm), silver (Ag) (80 nm), or lithium fluoride (LiF) (1 nm)/aluminum (Al) (100 nm) were thermally evaporated (pressure $< 10^{-6}$ mbar) as the top electrode.

When a metal is making intimate contact with a semiconductor or insulator, at equilibrium, the Fermi levels in two materials will coincide. If the work function of the metal is higher than the LUMO level of the semiconductor, an interface barrier ϕ_b for electrons will be formed [Fig. 2(a)]. As indicated in Fig. 2(a) for two of these blocking contacts, the V_{OC} of the device is given by difference between the metals work functions. For the PCBM devices a schematic diagram is shown in Fig. 2(a), where $M2$ is the bottom electrode (PEDOT:PSS, $\phi_{M2} = 5.2$ eV) and $M1$ is the evaporated top electrode (Ag, Au, LiF/Al). From Fig. 2(a) it appears that

$$\phi_b + qV_{OC} = \phi_{M2} - \text{LUMO}, \quad (1)$$

where q is electric charge, ϕ_b is electron barrier height, ϕ_{M2} is PEDOT:PSS work function (5.2 eV), and LUMO is the

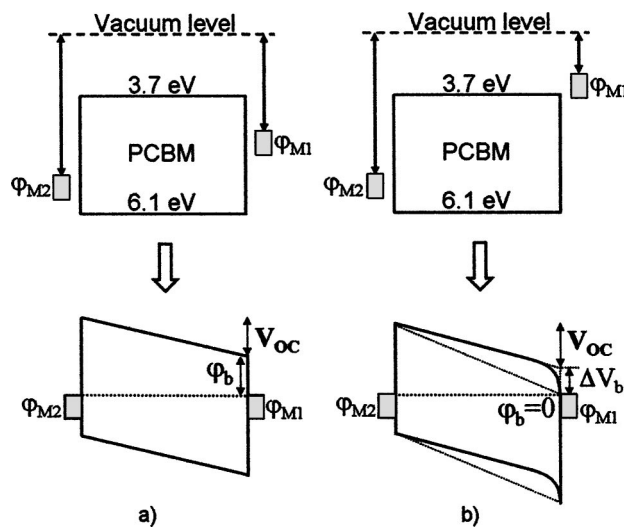


FIG. 2. Schematic band diagram of a metal-insulator-metal (MIM) device with non-ohmic contact for electrons and holes (a), and electron ohmic contact (b). Before metal contact (upper image) and after contact and under short-circuit condition (lower image). The ϕ_b and ΔV_b are injection barrier height for electrons at a non-ohmic contact and the voltage loss at an ohmic contact, respectively. ϕ_{M1} and ϕ_{M2} are the metal work functions.

position of the PCBM LUMO level with respect to vacuum (3.7 eV), respectively. Equation (1) indicates that for a given bottom electrode work function (in this case PEDOT:PSS), the sum of electron barrier height and V_{OC} is constant for different top electrodes. It is important to note that in our PCBM devices both the barrier height (ϕ_b) and V_{OC} can be independently determined from $J-V$ measurements. The barrier heights for electrons going from Ag and Au into the LUMO level of PCBM have been determined by investigation of the injection limited electron current (ILC).¹¹ It was recently demonstrated that the injection limited current is well described by hopping of charge carriers from the Fermi level of the metal into energetically disordered localized states of the organic semiconductor.^{9,10} According to this hopping-based model, the ILC is determined by four parameters;^{9,10} the energy width of the density of localized states σ , the nearest hopping distance a , the dielectric constant ϵ_r , and finally the energy distance from the Fermi level of the electrode to the center of the Gaussian DOS of the PCBM transport states (i.e., the barrier height ϕ_b). From the field and temperature dependence of the electron mobility of PCBM $\sigma = 0.073$ eV and $a = 3.4 \pm 0.1$ nm have been extracted.¹² Also, the dielectric constant of $\epsilon_r = 3.9$ has been found from impedance measurement. In Fig. 3, the calculated ILC of PCBM, according to the hopping based model, is plotted, together with experimental data, obtained at different temperatures. Using a barrier heights ϕ_b of 0.65 and 0.76 eV for Ag and Au, respectively, without any other free parameter, the calculated ILC is in a good agreement with the experimental results. Apparently, the injection barrier of the Au/PCBM contact is strongly reduced as compared to the band offset, from which a barrier of about 1.4 eV was expected. It has been demonstrated by ultraviolet photoemission spectroscopy (UPS) that at the Au/C₆₀ a strong interface dipole exists, which lowers the Au/C₆₀ interface barrier by

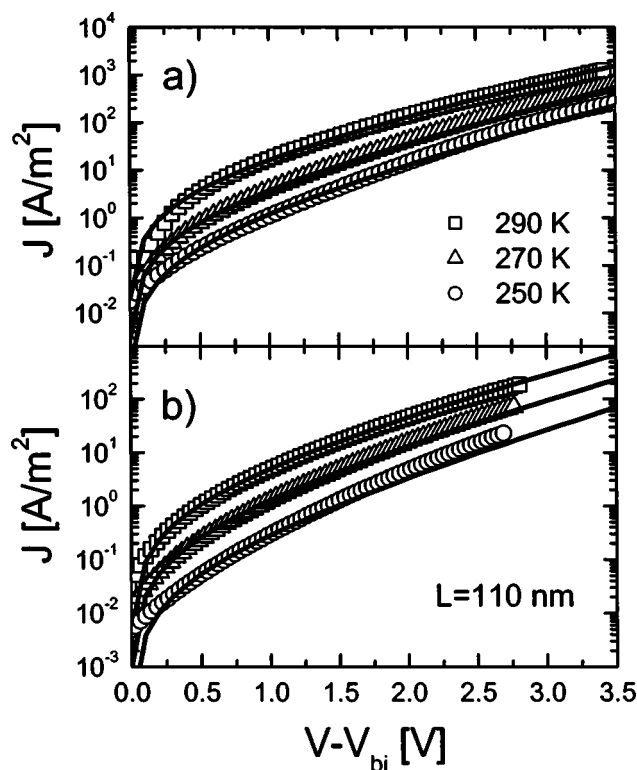


FIG. 3. Injection limited electron current (ILC) J vs V as a function of temperature (symbols) for an ITO/PEDOT:PSS/PCBM/top electrode device with thickness $L = 110$ nm. The top electrode is (a) Ag or (b) Au. The J - V characteristics, calculated according to the hopping model, are plotted as solid lines. The estimated built-in voltage V_{bi} has been subtracted from the applied bias.

0.64 eV.¹³ With the band offset of 1.4 eV this would give rise to an injection barrier of 0.76 eV, which exactly equals the barrier as extracted from the J - V measurements. This interface dipole is then responsible for the relatively large injection-limited electron current of the Au/PCBM contact, indicating that the Au work function is pinned at about 4.46 eV, in contact with PCBM. The Ag electrode is in the position (4.35 eV) where is expected from its work function, as was also demonstrated by UPS measurements.¹³

As a further control experiment, the J - V characteristics under illumination for ITO/PEDOT:PSS/PCBM/cathode devices with silver and gold cathodes were determined. These data are shown in Fig. 4. The relatively low photocurrent exhibited by the pure PCBM device is due to the poor light absorption in visible range. The obtained V_{OC} for Ag (0.84 V) and Au (0.74 V) were measured in the saturation regime (by checking at different light intensities). For both electrodes the sum of the barrier height (ILC measurements) and V_{OC} (photocurrent) equals 1.5 V, which in turn equals the energy distance between the Fermi level of the PEDOT:PSS (5.2 eV) and the LUMO of PCBM (3.7 eV), as predicted by Eq. (1). Thus the position of the metal Fermi level with respect to the LUMO level of PCBM is confirmed by two independent measurements.

The next issue to address is the situation in which the metal work function ϕ_{M1} is reduced to such an extent that it is even below the LUMO level of the semiconductor [as shown in Fig. 2(b)]. In this case, alignment of the Fermi

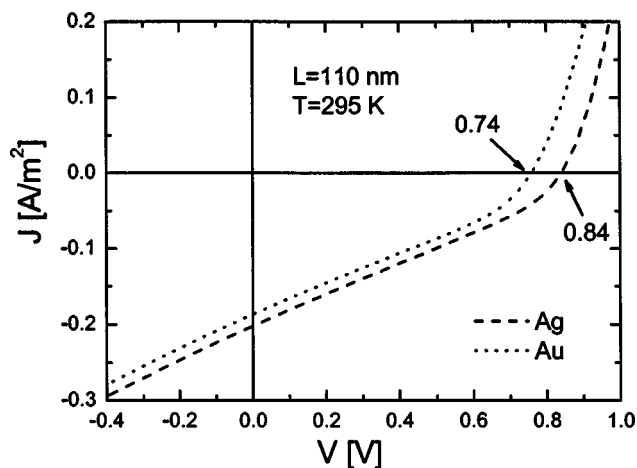


FIG. 4. J - V of ITO/PEDOT:PSS/PCBM/cathode devices, illuminated with a white light halogen lamp (80 mW/cm^2). The cathodes are silver (dashed line) and gold (dotted line). The device was illuminated through the glass substrate.

level is achieved by charge transfer of electrons from the metal into the semiconductor, and an ohmic contact is formed. As a result, the electrode work function becomes pinned close to the LUMO level of the semiconductor, as shown in Fig. 2(b).¹⁴ Furthermore, the accumulated charges at the interface will create a band bending, which leads to a reduction of the electric field in the bulk of the device.¹⁵ The resulting voltage loss, indicated by ΔV_b in Fig. 2(b), can be numerically calculated as a function of the barrier height ϕ_b , using a model by Simmons.¹⁶ In Fig. 5 the result is shown for a device with thickness $L = 95$ nm, at room temperature. It appears that for a barrier height $\phi_b > 0.25$ eV the voltage loss is negligible, since the barrier prevents the flow of electrons from the metal into the semiconductor. However, for $\phi_b < 0.25$ eV the contact becomes ohmic and for zero barrier, as shown in Fig. 2(b), a voltage loss of typically 0.2 V has to be taken into account. Thus, for an ohmic contact Eq. (1) is modified to:

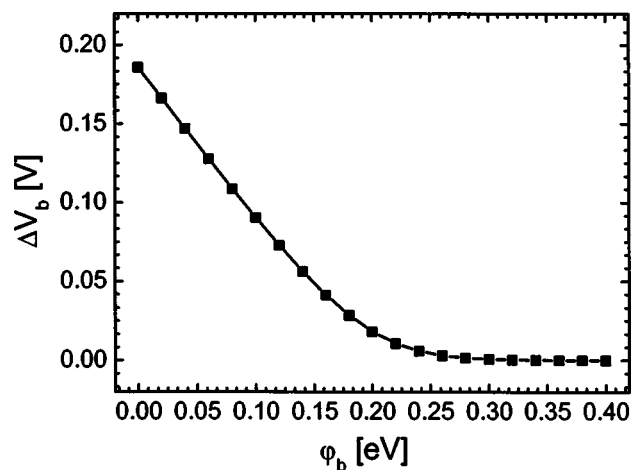


FIG. 5. Calculated voltage loss (ΔV_b) due to the band bending, as a function of the barrier height (ϕ_b), for an ohmic contact. The parameters used in calculation are thickness $L = 95$ nm, temperature $T = 295$ K, effective density of states in the conduction band $N_c = 3 \times 10^{20} \text{ cm}^{-3}$ and the dielectric constant $\epsilon_r = 3.9$.

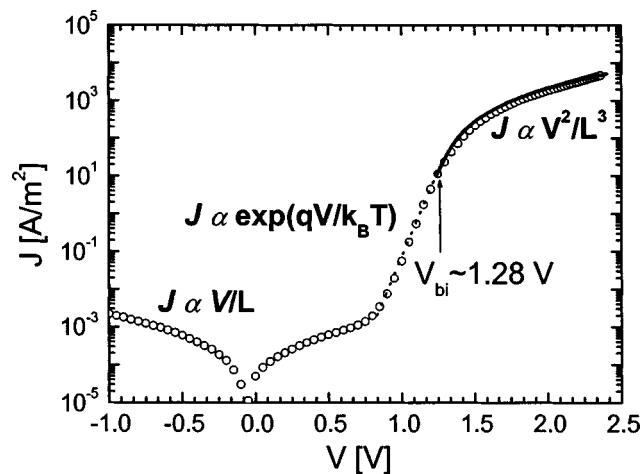


FIG. 6. Dark J - V characteristics (circles) of a PCBM-only device with thickness $L = 140$ nm, together with calculated exponential current (dotted line) and SCLC (solid line), at room temperature.

$$\varphi_b + qV_{OC} + q\Delta V_b = \varphi_{M2} - \text{LUMO}, \quad (2)$$

where ΔV_b , is the voltage loss due to the band bending at the ohmic contact.

The electron current injected from LiF/Al contacts was shown to be space-charge limited (SCL),¹² indicating that LiF/Al forms an ohmic contact for electron injection into the LUMO level of PCBM.^{8,12} As a result, the current is limited by the bulk properties of the PCBM layer and no information about the contact, like a barrier height, can be obtained from the J - V measurements. Furthermore, direct measurement of the V_{OC} by using the photocurrent of an ITO/PEDOT:PSS/PCBM/LiF/Al device was not possible due to the poor light absorption of the PCBM, leading to an unsaturated V_{OC} for this device. Thus the experimental methods used on the Ag and Au devices do not apply to the PCBM devices with LiF/Al contacts. However, it is possible to determine the built-in potential in the device directly from the J - V measurements. It should be noted that V_{OC} is an accurate estimate for the built-in potential at low temperatures, but at room temperature it might underestimate the built-in potential.⁷ In Fig. 6 the dark J - V characteristics of an ITO/PEDOT:PSS/PCBM/LiF/Al device is shown. It can be observed from Fig. 6 that the dark J - V characteristic of a PCBM device has three distinct regimes: At low voltage (0–0.8 V), the measured current is dominated by local leakage currents due to weak spots in the film, giving rise to ohmic behavior, which is symmetric for reverse bias. In the range 0.8–1.3 V, the current increases exponentially with voltage. In this regime the current is diffusion dominated, since the built-in electric field opposes the direction of the current. When the flat band condition is reached, the current becomes space charge limited (drift dominated).¹² Consequently, the built-in voltage can be read at the cross point between the exponential and SCLC regime, which amounts to $V_{bi} = 1.28 \pm 0.02$ V. This value can be taken as an upper limit for V_{OC} in this device, but does not provide accurate information about the band bending at the LiF/Al-PCBM contact.

The results of the PCBM-only devices are summarized in Table I. For non-ohmic contacts (Ag,Au) the sum of bar-

TABLE I. PCBM characteristics for φ_b , ΔV_b , and V_{OC} for different cathodes together with calculation values according to Eq. (2).

Cathode	φ_b (eV)	V_{OC} (V)	ΔV_b (V)	$\varphi_b + V_{OC} + \Delta V_b$ (eV)
LiF/Al	0	1.28 ^a		
Ag	0.65	0.84	0	1.49
Au	0.76	0.74	0	1.5

^aValue estimated from the built-in field (Fig. 6).

rier height and the V_{OC} of the device is constant, being the difference between work function of the bottom electrode and the LUMO level of PCBM. In the case of an ohmic contact the V_{OC} is reduced due to band bending as a result of accumulated charges. These results are relevant for the understanding of the open-circuit voltage of the polymer/fullerene BHJ solar cells, which will be addressed in the next section.

B. Open-circuit voltage of the OC₁C₁₀-PPV:PCBM blend device

With the position of the Fermi level of the Ag, Au, and LiF contact known, with regard to the LUMO of PCBM, the influence of the metal work function on the V_{OC} of conjugated polymer:fullerene BHJ solar cells is investigated. The active layer consists of a blend of conjugated polymer poly[2-methoxy-5-(3',7' dimethyloctyloxy)-phenylene vinylene] (OC₁C₁₀-PPV) used as the electron donor and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) as the electron acceptor. The PPV and PCBM was used in a ratio of 1:4 by weight and it was spin coated from a chlorobenzene solution on glass/ITO/PEDOT:PSS substrates. For the solar cells gold (Au), silver (Ag), palladium (Pd), or lithium fluoride (LiF=1 nm/aluminum (Al=100 nm) were thermally evaporated as a top electrode. The work function of PEDOT:PSS ($\varphi_{M2} = 5.2$ eV) matches the HOMO level of OC₁C₁₀-PPV (5.3 ± 0.1 eV), resulting in an ohmic contact for holes in the BHJ solar cell, under forward bias condition. On the other side, LiF/Al makes an ohmic contact for electron injection into the LUMO level of PCBM (3.7 eV). It should be stressed that for the PCBM-only devices with Au and Ag contacts, there is no band bending at either electrode, whereas for the solar cells with the same contacts there is additional band bending at the PEDOT/OC₁C₁₀-PPV interface. Furthermore, in the BHJ solar cell with a LiF/Al contact band bending occurs at both interfaces. For this particular device Eq. (2) modifies to:

$$q(V_{OC} + \Delta V_b) = \text{HOMO}_{\text{donor}} - \text{LUMO}_{\text{acceptor}}, \quad (3)$$

where ΔV_b is the sum of the voltage losses at each contact due to the band bending. Equation (3) shows that for two ohmic contacts the V_{OC} is given by the difference between the HOMO level of the donor (OC₁C₁₀-PPV) and the LUMO level of the acceptor (PCBM), minus the voltage losses at these contacts due to the band bending. Following the same approach as in PCBM only devices, we started with the investigation of the V_{OC} dependence on the metal work function with non-ohmic contacts.

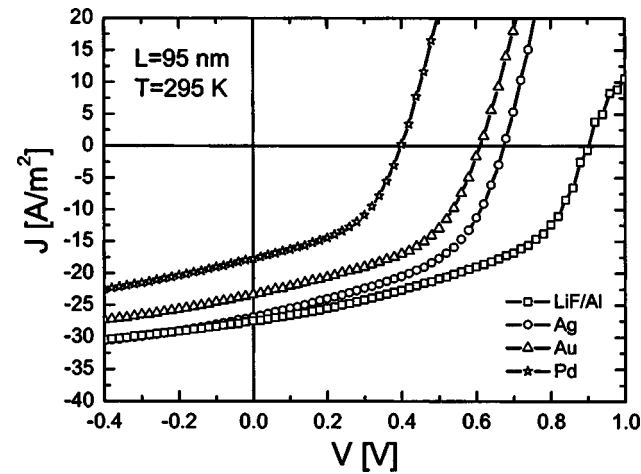


FIG. 7. J - V curves of ITO/PEDOT:PSS/OC₁C₁₀-PPV:PCBM (1:4 wt %)/cathode BHJ photovoltaic devices under illumination, with different metal electrodes (symbols). The device was illuminated with a halogen lamp with a power intensity of 80 mW/cm². The V_{OC} was found to be in saturation regime in all cases.

Figure 7 shows the J - V curves under illumination, of four typical ITO/PEDOT:PSS/OC₁C₁₀-PPV:PCBM/electrode BHJ devices using either LiF/Al, Ag, Au, and or Pd as the negative electrode. The measured V_{OC} values are summarized in Table II, together with values for the respective electron barrier heights (ϕ_b). As stated above, in the BHJ solar cells with Au and Ag contacts, there is additional band bending at the anode as compared to the PCBM-only devices. As a result, the difference in V_{OC} between the PCBM-only devices and the BHJ solar cells equals the voltage loss ΔV_b due to band bending at the ohmic hole contact. For both Au and Ag this difference amounts to 0.16 ± 0.02 V, which is the voltage loss due to band bending at the anode. This demonstrates that the solar cells with Ag and Au electrodes, when corrected for the band bending at the anode, behave as expected from the results of the PCBM only devices. Furthermore, the position of the Ag and Au electrode with regard to the LUMO of the PCBM is not modified by the presence of the polymer in the blend.

For the LiF/Al contact the situation is more complicated: the upper limit for the V_{OC} in a solar cell can be determined from the temperature dependence of V_{OC} .¹⁷ At $T=0$ K the diffusion of charges into the semiconductor and resulting

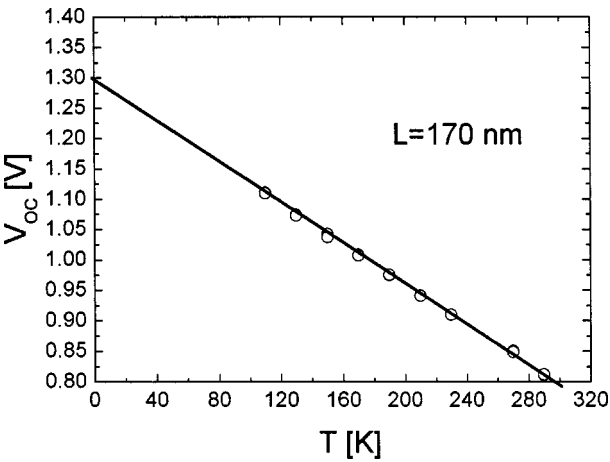


FIG. 8. V_{OC} as a function of temperature (symbols) for a device with active layer of OC₁C₁₀-PPV:PCBM. The solid line represents the linear extrapolation to $T=0$ K.

band bending are suppressed, and V_{OC} approaches its maximum value. In Fig. 8 the temperature dependence of V_{OC} is shown, and extrapolation to $T=0$ K gives a V_{OC} of 1.3 V, in agreement with an earlier reported result.¹⁷ However, from the HOMO-LUMO difference between OC₁C₁₀-PPV (5.3 eV) and PCBM (3.7 eV) an upper limit of 1.6 V for V_{OC} would be expected. The question is why this maximum V_{OC} amounts to only 1.3 V. It should be noted that the band diagrams as drawn in Fig. 2 assume a well defined band edge. However, both OC₁C₁₀-PPV and PCBM are disordered semiconductors, in which the charge transport is characterized by hopping in an energetically broadened Gaussian density of states (DOS). The widths of the Gaussian DOS σ for OC₁C₁₀-PPV and PCBM amount to 0.11 and 0.072 eV, respectively. The transport levels in the Gaussian DOS are located at $-5/9 \cdot \sigma^2/kT$ from the center,¹⁸ implying that for OC₁C₁₀-PPV and PCBM the transport levels are located 0.25 and 0.1 eV from the center of the DOS, respectively. Consequently, the HOMO(OC₁C₁₀-PPV)-LUMO(PCBM) distance of 1.6 eV, deduced from the maxim of the Gaussian DOS, is effectively reduced to about 1.25 eV, which corresponds closely to the maximum obtainable V_{OC} in the solar cells. Correcting the upper-limit of $V_{oc}=1.3$ V for the band bending at ambient temperature for two Ohmic contacts reduces the V_{oc} further to 0.9 V, which is in close agreement with the experimentally observed value.

In an earlier study⁷ using Ca, Ag, Al, and Au as cathodes, it has been demonstrated that the obtained variation in V_{OC} was less than 200 mV. Pinning of the Fermi level at PCBM surface states was suggested as a possible explanation. Also in our study the variation between LiF/Al, Ag, and Au is rather small. However, it is important to realize that the V_{OC} of cells with Al and Ag cathodes behave in correspondence with the MIM model, without an additional contribution by pinning. As we have shown, Ag is exactly at the position where it is expected from its work function. Furthermore, the Fermi level of LiF is pinned close to that of the LUMO of PCBM [shown in Fig. 2(b)] due to the accumulated charge carriers. Because of this pinning, the V_{OC} will

TABLE II. OC₁C₁₀-PPV:PCBM BHJ solar cells characteristics [V_{OC} ; total voltage loss due to ohmic contact (ΔV_b) as a function of different top electrodes; electron barrier heights (ϕ_b) are taken from the PCBM-only characteristics from Table I; $\phi_{M1} = \text{LUMO}_{\text{PCBM}} + \phi_b$ is the estimated effective metal work function, taking the barrier height into account].

Cathode	ϕ_b (eV)	V_{OC} (V)	ΔV_b (V)	ϕ_{M1} (eV)
LiF/Al	0	0.902		3.7
Ag	0.65	0.674	0.158	4.35
Au	0.76	0.59	0.158	4.46
Pd	0.944 ^a	0.398	0.158	4.644

^aValue calculated from Eq. (2): the measured V_{OC} from Fig. 7, taking into account the average voltage losses at the Ag and Au interfaces.

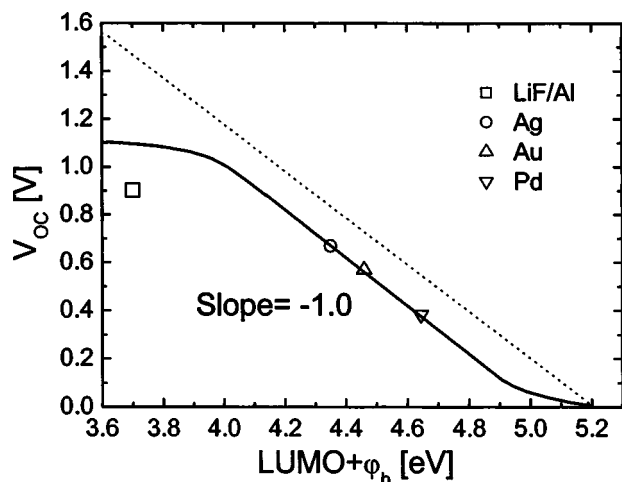


FIG. 9. V_{OC} as a function of effective position of the Fermi level of the negative electrode (symbols) for devices with OC_1C_{10} -PPV:PCBM active layer, at room temperature. The solid line represents the calculated value according to the MIM model. The dotted line indicates the linear dependence of V_{OC} with the acceptor strength of the fullerene.

be independent of the work function of the cathode whenever its work function is lower than the LUMO of PCBM. Therefore, cells with such electrodes, like Ca and LiF/Al, should not be included in the analysis of a work function dependence of V_{OC} . The only cell of which the measured V_{OC} strongly deviates from the MIM model is the one with the Au cathode. There are two possible explanations for its specific behavior: First, the energy level of Au at the PCBM interface is close to those of Ag and Al because all metals are pinned at that position due to the presence of a large number of interface states. The alternative is that Al and Ag are not pinned by surface states and that the energy level of Au by coincidence is at the same position because of a strong interface dipole.¹³ In order to discriminate between these options we also investigated the Pd electrode, which has a work function comparable to Au. As can be seen in Fig. 7, the V_{OC} of cells with a Pd electrode is strongly reduced to 0.39 eV. Although Pd is apparently shifted by 0.3 V with regard to its work function, a total variation of more than 0.5 V of the V_{OC} was observed by varying the negative electrodes. These results indicate that pinning of the metal Fermi level at a specific surface state of the methanofullerene is unlikely, but that Au is a special case because of its large interface dipole.

In Fig. 9 the results obtained in this study are summarized: the measured V_{OC} is plotted versus the position of the Fermi level of the negative electrode, given by $LUMO_{PCBM} + \phi_b$ as obtained from our measurements. The dashed line shows the behavior as expected from the MIM model.¹⁶ According to this model, V_{OC} increases linearly with the energy level of the cathode and then pins when the PCBM LUMO level at 3.7 eV is reached. The solid line represents the calculated V_{OC} when the voltage loss due to band bending at the anode interface (~ 0.2 V) is taken into account. For metals approaching the LUMO of PCBM, band bending at both interfaces (~ 0.4 eV) is taken into account. For cells with non-ohmic contacts, the observed V_{OC} is in agreement with

the expected values. In this case, V_{OC} is determined by the work function differences of the electrodes. However, for the ohmic contact the measured value of 0.9 V is lower than the predicted value of around 1.1 V, possibly due to the energetic disorder of the charge transport levels.

III. CONCLUSIONS

In conclusion we have shown that by variation of the negative electrode the open-circuit voltage of the polymer/fullerene BHJ solar cell varies by more than 0.5 V, which excludes the presence of a large amount of PCBM surface states. A clear distinction between ohmic and non-ohmic contacts was elucidated: for non-ohmic contacts the experimental V_{OC} is in agreement with the work function difference of the electrodes as expected from the MIM model. In case of ohmic contacts, the negative and positive electrodes match the LUMO of the acceptor and the HOMO of the donor, respectively, which govern the V_{OC} . Furthermore, the band bending at the ohmic contacts reduce the open circuit voltage by typically 0.2 V for each contact. These voltage losses strongly reduce the maximum attainable V_{OC} in an OC_1C_{10} -PPV:PCBM BHJ solar cell at room temperature.

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